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52 Method for producing a multilayer laminated sheet material carrying a decorative effect.

57 A method of producing a multilayer laminated sheet material carrying a decorative effect comprises the steps of applying to one side of a sheet of transparent thermoplastic material, preferably polymethyl methacrylate, to constitute a two layer assembly having a decorated side, material providing a decorative effect; adhesively applying to the decorated side of the two layer assembly a coating of a composition comprising uncured acrylic material; allowing or causing said coating to cure to provide a protective overcoat covering the material providing the decorative effect; adhesively applying to the protective acrylic overcoat a coating comprising a solution of an acrylate polymer in a difunctional acrylic monomer and a low viscosity polyester resin; allowing or causing the latter coating to cure to provide a further layer; adhesively applying to said further layer a glass fibre reinforced plastic (GRP) composition comprising styrene monomer, polyester resin and glass fibre; and allowing or causing the latter composition to cure to provide a glass fibre reinforced plastics layer.

The multilayer laminated sheet may be flat or may be shaped, e.g. as a bath or washbasin with the decorative effect visible on the concave side. Shaping is carried out before the application of the GRP layer and preferably before the application of the material providing the decorative effect.

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TITLE MODIFIED

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Multilayer Laminated Plastic Sheet Material

TECHNICAL FIELD OF THE INVENTION

The present invention relates to multilayer laminated plastic sheet material carrying a visual decorative effect, a method of producing such material and articles made from such material.

BACKGROUND OF THE INVENTION

It is known to produce shaped articles, such as baths and washbasins by vacuum forming thermoplastic sheets, such as polymethyl methacrylate sheets, commonly 3 to 8 mm thick and applying a reinforcing backing layer of glass-fibre reinforced plastic (GRP) over the vacuum-formed sheet.

The present inventors have attempted to produce multilayer laminated sheet material comprising: a transparent thermoplastic sheet, for example of polymethyl methacrylate; material providing a decorative effect applied to one side of the transparent thermoplastic sheet; a protective overcoat of acrylic material applied to the material providing the decorative effect and said one side of the transparent thermoplastic sheet; and a reinforcing stiffening backing layer of glass-fibre reinforced plastic (GRP) applied to the overcoat. The GRP is made from a composition comprising, in addition to glass fibre, an unsaturated polyester resin which is, for example, a resin made from 1 mol of phthalic anhydride, $\frac{1}{2}$ mol of maleic anhydride and $1\frac{1}{2}$ mol of 1,2-propylene glycol, the

resin being dissolved in styrene monomer in the proportion of 2 parts by weight of resin to 1 part by weight of styrene.

5 In the manufacture of such sheet material, the unsaturated polyester resin is activated with catalyst and accelerator and a coating of the activated resin is applied to the protective acrylic overcoat. The unsaturated polyester resin, after its application to the protective overcoat, cures in situ and is touch
10 hard in only a few minutes. However, the resin takes hours to become substantially cured throughout the thickness of the coating. Thus, during the curing of the resin, there is a considerable amount of styrene monomer in contact with the protective overcoat for a
15 substantial time. There is a tendency for the styrene monomer to diffuse into and through the protective overcoat. Diffusion of the styrene monomer through the protective overcoat can result in marring of the decorative effect. Also, diffusion of the styrene
20 monomer into the protective overcoat can substantially reduce the heat distortion temperature of the protective overcoat thereby making the multilayer laminated sheet material unsuitable for use where it will be subjected to elevated temperatures, for example for
25 use in baths and washbasins.

DISCLOSURE OF THE INVENTION

The present invention enables the above-described disadvantages to be overcome.

30 The present invention resides in the provision of an intermediate layer between the protective overcoat and the GRP layer, the intermediate layer preventing or at least inhibiting penetration of the protective overcoat by styrene monomer from the composition which cures to form the GRP layer, the intermediate
35 layer being adherent to both the protective overcoat and the GRP layer. The intermediate layer is made by

curing in situ a coating of a composition comprising an acrylate polymer in a difunctional acrylic monomer (i.e. an acrylic monomer having a single carbon-carbon double bond in the molecule) and a low viscosity polyester resin, such as Crystic Resin 189LV (Scott Bader Co. Ltd) of viscosity 3.6 poises at 25°C.

Thus, in accordance with the present invention, there is provided a method of producing a multilayer laminated sheet material carrying a decorative effect comprising: adhesively applying to one side of a sheet of transparent thermoplastic material, to constitute a two layer assembly having a decorated side, material providing a decorative effect; adhesively applying to the decorated side of the two layer assembly a coating comprising uncured acrylic material; allowing or causing said coating to cure to provide a protective acrylic overcoat covering the material providing the decorative effect; adhesively applying to the protective acrylic overcoat a coating comprising a solution of an acrylate polymer in a difunctional acrylic monomer and a low viscosity polyester resin; allowing or causing the latter coating to cure to provide a further layer; adhesively applying to said further layer a glass-fibre reinforced plastic (GRP) composition comprising styrene monomer, polyester resin and glass fibre; and allowing or causing the latter composition to cure to provide a glass-fibre reinforced plastic (GRP) layer. Customary catalyst/accelerator systems are used in the curing operations above.

The protective overcoat and/or the further layer and/or the glass fibre reinforced plastic layer may be clear or pigmented to provide opacity to the laminated sheet material.

Said further layer thus constitutes, in the multilayer laminated sheet material produced, a layer intermediate the protective acrylic overcoat and the

GRP layer and is herein referred to as the "intermediate layer" whether or not the GRP layer has been applied to it.

5 It will be appreciated that the composition to form the intermediate layer and the composition which forms the protective acrylic overcoat layer each comprise at least one acrylic component and the composition to form the intermediate layer and the composition to form the GRP layer each comprise at
10 least one polyester component. The intermediate layer thus constitutes a seal resistant to styrene monomer and which is adherent to both the protective acrylic overcoat and the GRP layer.

By a "low viscosity polyester resin", is meant
15 polyester resin having a viscosity no higher than 5 poises.

The low viscosity polyester resin in the composition to form the intermediate layer may be Crystic 189 IV, as hereinafter described.

20 The composition to form the intermediate layer usually comprises an accelerator and catalyst. Also, the composition usually comprises a thixotropic agent and may comprise pigment.

The low viscosity polyester resin of the
25 composition to form the intermediate layer is preferably based on phthalic anhydride, maleic anhydride and propylene glycol, the resin being made with a slight excess of the glycol or the phthalic anhydride such that the polyester resin molecules are end
30 stopped and the degree of polymerization is consequently low. When such a resin is dissolved in styrene in the ratio 1 part by weight of styrene monomer to 2 parts by weight of resin, a low viscosity syrup is obtained. Such resins, wherein the degree of
35 polymerization is low, are often described as having

a long green time and are such that, when used in laminating considerable time may be allowed to lapse between application of the resin to one lamina and application of another lamina to the resin without
5 impairment of the interlamina bond.

The composition to form the intermediate layer optionally comprises a tetra(or higher)functional acrylic monomer such as glycol dimethacrylate.

The transparent thermoplastic material is
10 preferably an acrylic material, more preferably polymethyl methacrylate. Alternatively, the transparent thermoplastic material may be another transparent thermoplastic material such as polystyrene, polyvinyl chloride, cellulose acetate, cellulose acetate butyrate,
15 polyethylene, polypropylene, ethylene copolymer or polycarbonate, provided that the transparent thermoplastic material has a surface which is intrinsically receptive to the coating from which the protective acrylic overcoat is formed or has a receptive
20 surface of this nature developed by mechanical or chemical treatment or corona discharge.

Preferably, the sheet of transparent thermoplastic material has a thickness of at least one millimetre.

The decorative effect may be of one colour or
25 of many colours, discontinuous, in the form of one plain colour, a variegated all over colour, an all over patterned effect or one or more individual items such as monograms, escutcheons or flower motifs.

The material providing the decorative effect may
30 be a printing ink and may be applied for example by silk screen printing, transfer printing, stencilling, painting, spraying or rolling.

The printing ink must be such that it adheres to the transparent thermoplastic material and is not
35 adversely affected by the protective acrylic overcoat.

If the thermoplastic sheet material is to be shaped by vacuum forming after the application of the decorative effect, the printing ink must be such that, when it has been applied to the thermoplastic sheet material, it is capable of stretching without adverse effects such as fissuring, cracking and adhesion failure.

Where the transparent thermoplastic material is an acrylic material, a suitable vehicle for the printing ink is made from an acrylic monomer such as methyl methacrylate, methyl acrylate, butyl methacrylate or a mixture of such monomers, thermoplastic acrylic polymer such as polymethyl methacrylate, polybutyl methacrylate or polymethyl acrylate, and acrylic monomer containing two or more double bonds per molecule, such as glycol or polyglycol diacrylate or dimethacrylate or trimethylol propane tri methacrylate. Additionally a thickening agent such as a low viscosity ethyl cellulose or cellulose acetate butyrate may be included.

The purpose of the thermoplastic acrylic polymer is to give body to the vehicle. The purpose of the monomer containing two or more double bonds is to effect cross-linking when the ink is applied so that the decorative effect obtained is not adversely affected subsequently by the protective acrylic overcoat.

Another suitable vehicle for the printing ink, where the transparent thermoplastic material is polymethyl methacrylate, is made from unsaturated polyester, made for example by reacting 1 mol of phthalic anhydride, $\frac{1}{2}$ mol of maleic anhydride and $1\frac{1}{2}$ mols of propylene glycol together to give an unsaturated polyester resin which is diluted with styrene in the proportion of about 2:1.

A further suitable vehicle for the printing ink, where the transparent thermoplastic material is polymethyl methacrylate, is made from liquid epoxy

resin made from Bisphenol A (diphenylol propane) and epichlorhydrin, optionally plasticized with n.butyl glycidyl ether, then modified by reaction with monomeric acrylamide or acrylic acid.

5 Acrylic acid or methacrylic acid may be optionally included in the above-described vehicles in order to promote adhesion to the polymethyl methacrylate.

Colorants are added to the above-described vehicles to give printing inks.

10 All the above-described vehicles are set by double bond polymerization. This may be achieved by adding an accelerator/catalyst system consisting of, for example, dimethyl aniline/benzoyl peroxide so that the printing ink can be cold cured or more rapidly heat
15 cured. Alternatively, the printing ink may be cured by radiation, e.g. ultraviolet radiation. Where the printing ink vehicle is cured by ultraviolet radiation, an ultraviolet sensitizer, such as benzoin, is preferably included in the printing ink.

20 Alternatively, the material providing the decorative effect may be gold leaf. Gold leaf may be applied by means of a pressure die, the surplus peeled off and the applied design overcoated with the protective layer.

25 As a further alternative, the material providing the decorative effect may be plastic foil applied by hot foil printing. In hot foil printing, plastic foils of uniform or variegated colour, including metallic colours, are pressed onto the transparent
30 thermoplastic sheet by means of heated dies, any surplus is removed and the applied design is overcoated with the protective layer. By the use, for example, of a silver foil, a bath with a reflecting mirror over part or all of its concave surface is
35 produced. Intaglio designs may be produced on the surface of the polymethyl methacrylate sheets by hot

pressing with a heated die, or by engraving. The intaglio design thus produced is filled with a curing pigment paste by wiping. The coloured intaglio designs thus produced are overcoated with the protective layer.

5 For those decorative effects that are applied to the surface of the transparent thermoplastic sheet, improved adhesion of the decorative layer is obtained by pretreating the area of the sheet to which the decorative effect is to be applied, by abrasion with,
10 for example, fine glass paper. Then, after the design has been applied, the whole of the area that was abraded is given an overcoat of acrylic lacquer to restore the original transparency of the sheet.

The composition to form the protective acrylic
15 overcoat comprises a vehicle and, preferably, an opacifying agent. The vehicle is preferably made from one or more acrylic monomers such as methyl methacrylate, methyl acrylate, butyl methacrylate and polybutyl methacrylate dissolved in the monomer to give body
20 to the coating, and acrylic monomer containing two or more double bonds per monomer molecule, such as glycol or a polyglycol diacrylate or dimethacrylate or trimethylol propane trimethacrylate. Where the transparent thermoplastic material is polymethyl
25 methacrylate, acrylic acid and/or methacrylic acid is preferably present in the vehicle of the composition to form the protective overcoat in order to promote adhesion to the polymethyl methacrylate and optionally the material providing the decorative effect.

30 An accelerator/catalyst system is preferably included in the vehicle of the composition to form the protective acrylic overcoat. In the application of the protective acrylic overcoat, the accelerator/catalyst system is optionally so adjusted that the
35 heat released by the exothermic polymerization reaction is enough to raise the temperature of the adjacent surface of transparent thermoplastic sheet

(i.e. the surface to which the decorative effect has been applied) and the material of the applied decorative effect so that adhesion of the latter material to the thermoplastic material is promoted, but not to such a degree that the said surface of the thermoplastic material and the applied decorative effect are adversely affected.

The composition to form the protective acrylic overcoat may comprise one or more colorants to render the protective acrylic overcoat coloured.

The composition forming the protective acrylic overcoat is preferably applied by spraying or painting.

The protective acrylic overcoat is preferably 0.1 to 2 mm thick.

The protective acrylic overcoat, when pigmented, serves to render the multilayer laminated sheet opaque when viewed from the side of the transparent thermoplastic material and to protect the decorative effect from damage.

Where the transparent thermoplastic material is to be vacuum formed, after application of the material providing the decorative effect and the protective acrylic overcoat, it is necessary that the protective acrylic overcoat be able to stretch without defects occurring during the vacuum-forming.

The glass-fibre reinforced plastic layer comprises a resin binder component and a glass fibre component. The resin binder component may comprise unsaturated polyester resin. A suitable unsaturated polyester resin is made from phthalic anhydride, maleic anhydride and propylene glycol and, the resin component is diluted with monomeric styrene. In order to promote adhesion, part of the styrene may be replaced by acrylic acid or methacrylic acid.

The polyester resin may be a plasticized polyester resin.

A suitable plasticized polyester resin is obtained by using an unsaturated polyester resin of high acid value, that is one in which the linear polyester molecules are terminated by carboxy groups. In use, this resin is diluted with monomeric styrene, for example in the ratio of 2 resin:1 styrene. A polyurethane rubber precursor is added, for example one of the Adiprenes. The Adiprenes are a series of liquid polyurethane rubber precursors supplied by E.I. Du Pont de Nemours & Co. (Inc.). They are believed to be isocyanate bearing polyethers, and to contain terminal and side chain isocyanate groups. Adiprenes have Brookfield viscosities at 30°C ranging from about 6,000 to 20,000 cps and isocyanate contents ranging from about 2.8 - 9.5%. The normal methods of curing the Adiprene precursors is by reaction with polyamines such as MOCA, i.e. 4,4 -methylene bis (2-chloro aniline), or with polyols such as butane diol or trimethylol propane. In addition to its reaction with the amine group and the hydroxyl group, the isocyanate group will also react with the carboxy group. The calculated amount of the Adiprene added is that which contains enough isocyanate groups to react with the free carboxy groups on the polyester resin. To the above mixture consisting of unsaturated polyester resin of high acid value, styrene monomer and Adiprene, additions are made of a catalytic amount of dibutyl tin dilaurate for the isocyanate/carboxy group reaction and the amine peroxide catalyst system for the polymerisation reaction of unsaturated polyester resin.

A liquid epoxy resin made for example from Bisphenol A and epichlorhydrin and optionally n.butyl glycidyl ether as plasticizer, modified by reaction with monomeric acrylamide or acrylic acid may be used in GRP in place of polyester resin. The usual double bond accelerator/catalyst curing system is used.

The glass fibre component may be chopped glass fibre strands.

The glass-fibre reinforced plastics layer may also incorporate particular filler.

5 Before the GRP layer is applied and before or after application of the intermediate layer, the transparent thermoplastic sheet may be shaped for example by vacuum-forming.

10 Where the transparent thermoplastic sheet is to be shaped, it is preferred to shape the transparent thermoplastic sheet before the application thereto of the material providing the decorative effect. This eliminates problems which might otherwise arise due to distortion of the decorative effect as a result
15 of the decorative effect also being shaped.

In order to assist adhesion of the material providing the decorative effect and the protective acrylic overcoat to the transparent thermoplastic material, the surface of the transparent thermoplastic
20 material may be given a pretreatment. Such pretreatment may comprise mild abrasion or, where the transparent thermoplastic material is polymethyl methacrylate, a wipe-over with an active liquid such as methyl methacrylate monomer, methacrylic acid
25 monomer or dichloromethane.

EXAMPLES OF THE INVENTION

The invention is illustrated by the following examples.

Example 1

30 To one side of a transparent sheet of polymethyl methacrylate having a thickness of 3 to 5 mm, there was applied, by a conventional silk screen printing technique, a printing ink to provide a decorative effect in the form of a repeating pattern of motifs.

35 The printing ink had the following composition:

Solution A

Parts by Weight

| | |
|---|-----------|
| Liquid epoxy resin (Shell Chemicals 828) | 22.5 |
| Xylene | 10 |
| Methyl ethyl ketone | 10 |
| Pigment | 0.25 to 5 |

Solution B

| | |
|--|-----|
| Liquid polyamide resin (reaction product of dilinoleic acid with ethylene diamine) | 7.5 |
| Xylene | 10 |
| Methyl ethyl ketone | 10 |
| Cyclohexanol | 8.5 |

These solutions, A and B, are mixed together before use.

The applied printing ink cures to a hard film in 5 to 10 hours at room temperature; curing is speeded up by heating at 50°C, for example.

Over the printing ink and the polymethyl methacrylate sheet there was applied a coating of a composition comprising uncured acrylic material.

The ingredients of the composition were as follows:

Parts by Weight

| | |
|--|-----|
| Polymethyl methacrylate (low molecular weight lacquer grade) | 17 |
| Glycol dimethacrylate | 2.5 |
| Methyl methacrylate | 83 |
| Pigment paste (80% pigment and 20% liquid unsaturated polyester) | 10 |
| (Pigment is commonly titanium dioxide) | |
| Benzoyl peroxide | 5 |
| Dimethyl paratoluidene | 2 |
| Finely divided silica (Aerosil) | 2.5 |

300 grams per square metre.

The coating composition was cured by being maintained at room temperature for two hours to form an opaque protective overcoat having a thickness of 0.3 mm.

Over the opaque protective overcoat there was applied a lacquer. The lacquer had been prepared by mixing the following components together in the stated amounts.

- 10 19 parts by weight Elvacite (a readily soluble medium molecular weight polymethyl methacrylate)
- 81 parts by weight methyl methacrylate monomer
- 2½ parts by weight glycol dimethacrylate
- 10 parts by weight pigment paste (approx 50/50 weight pigment/carrier)
- 15 2½ parts by weight Aerosil 100 (thixotropic silica powder)
- 5 parts by weight benzoyl peroxide
- 2 parts by weight dimethyl paratoluidine

- 20 Then 41 parts by weight of Crystic 189 LV are added to form a lacquer. (Crystic 189V is a polyester resin based on phthalic anhydride, maleic anhydride and propylene glycol, the resin being made with a slight excess of the glycol or the phthalic anhydride such
- 25 that the polyester resin molecules are end-stopped by acetylation or esterification, respectively, and the degree of polymerization is consequently low. The resin has a viscosity of 3.6 poises at 20°C.)

- 30 With reference to the example above, it is believed that the acrylic component or components of the intermediate coating serve to give it good adhesion to the acrylic protective overcoat. Also, we believe that the relatively large amount of benzoyl peroxide in the intermediate coating, besides giving a considerable exothermic reaction and hence a quick cure,
- 35 ensure that substantially all of the styrene monomer in the intermediate coating becomes polymerized. In

the example, the benzoyl peroxide content is about 4% of the weight of the polymerisable material. A typical amount in general practice is 1 to 2%. Also, it is believed that the intermediate coating although

5 substantially resistant to styrene monomer, is penetrated sufficiently to ensure good adhesion of the GRP layer.

The coating of the lacquer was applied to the acrylic protective overcoat at a thickness of 1 mm, that is at about 1,000 g/m². The coating was cured, that is cross-linked, at room temperature in about six minutes to form the intermediate layer, and then a reinforcing stiffening backing layer of GRP was applied to the intermediate layer constituted by the

10 cured lacquer.

The GRP layer had the following composition and cured in about ten minutes at room temperature.

| | <u>Parts by Weight</u> |
|------------------------------|------------------------|
| Unsaturated polyester | 2 |
| Chopped glass strand | 1 |
| Methyl ethyl ketone peroxide | 1.5 to 2 |
| Cobalt naphthenate | 0.5 |

The decorative effect was not adversely affected during the application and curing of each of the subsequently applied layers.

20

The multilayer laminated sheet produced by the above described method was in the form of a flat panel.

Example 2

The method of Example 1 was repeated with the modification that the transparent thermoplastic sheet was subjected to shaping by vacuum forming before the application of the printing ink and all other layers. By this method baths and washbasins were formed, the baths and washbasins having their inner, concave

25 surfaces provided by the polymethylmethacrylate. The

30

decorative effect, which was thus visible on the inner, concave surfaces of the baths and washbasins was not adversely affected by the processing subsequent to its application.

CLAIMS

1. A method of producing a flat or shaped multi-layer laminated sheet material carrying a decorative effect, characterised by the steps of:-

5 adhesively applying to one side of a sheet of transparent thermoplastic material, to constitute a two layer assembly having a decorated side, material providing a decorative effect;

10 adhesively applying to the decorated side of the two layer assembly a coating of a composition comprising uncured acrylic material;

allowing or causing said coating to cure to provide a protective acrylic overcoat covering the material providing the decorative effect.

15 adhesively applying to the protective acrylic overcoat a coating comprising a solution of an acrylic overcoat a coating comprising a solution of an acrylate polymer in a difunctional acrylic monomer and a low viscosity polyester resin;

20 allowing or causing the latter coating to cure to provide a further layer;

25 adhesively applying to said further layer a glass-fibre reinforced plastic (GRP) composition comprising styrene monomer, polyester resin and glass fibre; and

allowing or causing the latter composition to cure to provide a glass-fibre reinforced plastic layer.

2. A method, according to Claim 1, wherein the
30 composition to form the further layer includes an accelerator and a catalyst.

3. A method, according to either preceding claim, wherein the composition to form the further layer includes a thixotropic agent.

4. A method, according to any preceding claim,
5 wherein the composition to provide the protective overcoat includes pigment.

5. A method, according to any preceding claim, wherein the composition to provide the further layer includes pigment.

10 6. A method, according to any preceding claim, wherein the composition to provide the glass-fibre reinforced plastic layer includes pigment.

15 7. A method, according to any preceding claim, wherein the polyester resin in the composition to form the further layer is based on phthalic anhydride, maleic anhydride and propylene glycol, the resin being made with a slight excess of the phthalic anhydride or the propylene glycol such that the polyester resin molecules are end-stopped.

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8. A method, according to any preceding claim, wherein the transparent thermoplastic material is a transparent thermoplastic acrylic material.

9. A method according to Claim 8, wherein the
5 transparent thermoplastic material is polymethyl methacrylate.

10. A method, according to any preceding claim, wherein the material providing the decorative effect is a printing ink.

10 11. A method, according to Claim 10, as appendent to Claim 8 or Claim 9, wherein the printing ink comprises, as vehicle, acrylic monomer having one double bond per molecule, thermoplastic acrylic polymer and acrylic monomer having two double bonds per
15 molecule.

12. A method, according to Claim 10 as appendent to Claim 8 or Claim 9, wherein the printing ink comprises, as vehicle, a solution of unsaturated polyester in styrene.

13. A method, according to Claim 10 as appendent
to Claim 8 or Claim 9, wherein the printing ink com-
prises, as vehicle, liquid epoxy resin made from
diphenylol propane and epichlorhydrone modified by
5 reaction with acrylamide or acrylic acid.

14. A method, according to any one of Claims 10
to 13, wherein the printing ink vehicle includes
acrylic acid or methacrylic acid.

10 15. A method, according to any one of Claims 1
to 14, wherein the transparent thermoplastic material
is shaped before application of the material providing
the decorative effect.

15 16. A method, according to any one of Claim 1
to 14, wherein the transparent thermoplastic material
is shaped before the application of the GRP composition.

17. A method, according to Claim 15 or Claim 16,
wherein the shaping is effected by vacuum forming.



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EUROPEAN SEARCH REPORT

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Application number

EP 78 30 0149

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | CLASSIFICATION OF THE APPLICATION (Int. Cl.) |
|--|---|-------------------------|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | |
| | <p><u>FR - A - 1 548 940 (DU PONT)</u> (06-12-1968)</p> <p>* Abstract pts. 1-4, a-d, 8, 9, 14-18; page 2, example 1, 2, 4, 5, 7 *</p> | 1, 2, 4, 5, 7-11, 15-17 | B 44 C 5/04 B 29 D 3/02 B 32 B 17/06 |
| | <p><u>GB - A - 1 472 150 (TOPLA)</u> (04-05-1977)</p> <p>* Claims 1, 8-10; page 1, line 81 - page 3, line 60; figure 3, A-D *</p> | 1, 5, 8-11, 15, 17 | |
| | <p><u>FR - A - 2 259 866 (PLASTIMER)</u> (29-08-1975)</p> <p>* Claims 1, 4, 6, 8, 9, 11; page 2, line 17 - page 4, line 36; example 1 *</p> | 1, 2, 7-9 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.) |
| | | | B 32 B B 29 D 3/02 |
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| The present search report has been drawn up for all claims | | | |
| Place of search | Date of completion of the search | Examiner | |
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